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# Silicon nanoclusters embedded in $SiO_2$ studied by Raman scattering

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**Abstract.** Low concentration of nanometric sized particles produced by a ball milling procedure were introduced into $SiO_2$ matrix by the sol-gel method. $SiO_2$ sol-gel formulations with high water-TEOS ratios were prepared. Samples with high silanol concentration was obtained for high temperatures as was proven by FTIR spectroscopy measurements. Raman scattering measurements showed evidence of a photo-oxidation effect of Si nanoparticles embedded into a $SiO_2$ matrix. Si particle sizes measured by Raman scattering were in the range from 7 to 14 nm.

## 1. Introduction

Si nanoparticles embedded into a $SiO_2$ matrix has been a goal for several researchers in the last years. The main interest to obtain these systems is the study of the light emission properties of Si when it is in a nano-sized structure. Among the different procedures used to obtain these systems are implanting Si atoms into $SiO_2$ matrix [1], reactive RF magnetron sputtering [2], Low Pressure Chemical Vapor Deposition (LPCVD) [3]. L. Zhang *et al* reported an interesting procedure to obtain Si nanoparticles into a sol-gel $SiO_2$ matrix, introducing Si particles from porous Si [4]. However, the materials obtained are instable, so that the initial light emission decreases with time and disappears. In this work we are introducing Si particles into $SiO_2$ by using a sol-gel solution with high water-TEOS ratio. It was introduced a milling process [5] by using a low energy ball mill, with the goal of study the effect of dispersion on the retention of water into the $SiO_2$ matrix. During the gelation process, the partially oxidized Si particles are covered by the $SiO_2$ material. The samples were studied by infrared and Raman scattering measurements.

## 2. Experimental

Preparation of small particles of Si: By using a high energy ball mill, granular silicon was milled to reduce its grain size. The weight ratio balls/silicon was of 2:1. The milling process was achieved in typical time of 30 min. 1.0 g of this milled powder was incorporated into an acidified solution of ethanol, $HNO_3$ and water, and reposed by 24 hours. The precipitated powder was separated from the mixture by a decanting process. This suspension was used to prepared the precursor formulations of $SiO_2$ with Si. Preparation of suspensions for $SiO_2$ matrix with Si particles the sol-gel solution precursor of the $SiO_2$ was prepared mixing during 15 minutes, by using a magnetic stirrer, the suspension with silicon particles and TEOS (tetraethyl-orthosilicate) in a molar ratio of 4:1. After this process, it was added water in a molar ration respect to TEOS of 17:1. The suspension was milled in a low

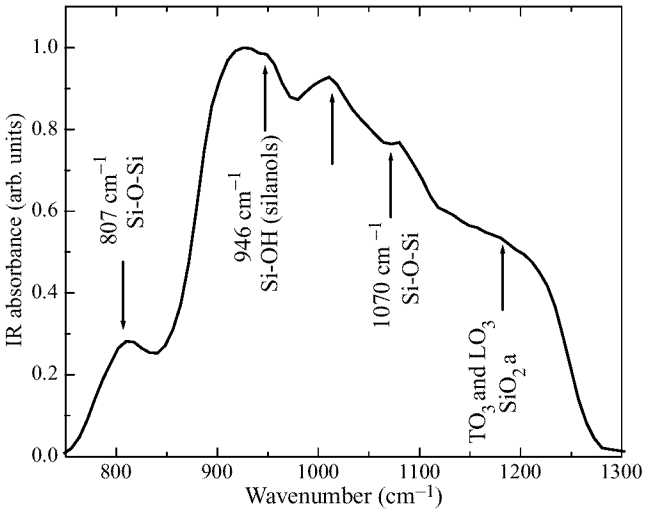


**Fig. 1.** IR spectrum for the $SiO_2$:Si sample, for the range from 750 to 1300 cm$^{-1}$, for a $SiO_2$-Si milled suspension after a thermal annealing at 500°C by 1.0 h.

energy ball mill. Dried samples were thermal annealed at 500°C of temperature. The experimental techniques used to analyze the samples were infrared spectroscopy (NICOLET mod. AVATAR 360-FTIR) in the diffuse reflectance mode and Micro-Raman (DILOR). For micro-Raman measurements the samples were exposed to two light intensities (20 and 5 mW by using a filter), and sequential periods of time. The laser light was focused to 1.0 $\mu$m$^2$ of area.

In Figure 1 there is shown an IR spectrum, in the range from 750 to 1300 cm$^{-1}$, of the $SiO_2$:Si sample. Five broad bands can be observed from this figure. These bands can be identified as vibrational modes of $SiO_2$ [6] and Si-OH (silanol) [7]: bending mode O-Si-O ~819 cm$^{-1}$ ($\delta$), stretching mode Si-O ~1070 cm$^{-1}$, stretching Si-OH ~930 cm$^{-1}$, and TO and LO modes of O-Si-O ~1100–1250 cm$^{-1}$ [8, 9]. An additional band is observed for about 1030 cm$^{-1}$, this band has been attributed for structural order in the amorphous $SiO_2$ [10]. The position of these modes are signed in the figure by vertical arrows.

Powder samples were exposed to light bath for several periods of time, by using a 632 nm He-Ne laser (5–20 mW output power focused on 1.0 $\mu$m$^2$ of area) during the Raman Measurements. Figure 2 shows the Raman spectra for the sample for two case: (a) changing the focus distance from 0 to 10 $\mu$m in steps of 2.5 $\mu$m and, (b) measuring after exposition to variable laser light intensity and exposition time. Curves signed as A, B, C, and D, respectively, correspond to sample exposition of 6 (A), 9 (B), 12 (C) and 15(D) min with light intensity of 5 (A), 5 (B), 20 (C) and 20 (D) mW, respectively. The continuous line corresponds to the best fitting of the experimental data to a model [11] that considers spherical Si grains (see in figure). After 6 min of light exposition there is a shift of the peak for about 3 cm$^{-1}$ that can be attributed to an temperature increase of the Si grains.

## 3. Discussion and Conclusions

Raman spectra for several light exposition times and variable effective power, of the $SiO_2$:Si sample showed an interesting effect of reduction of effective Si grain size. This sample has

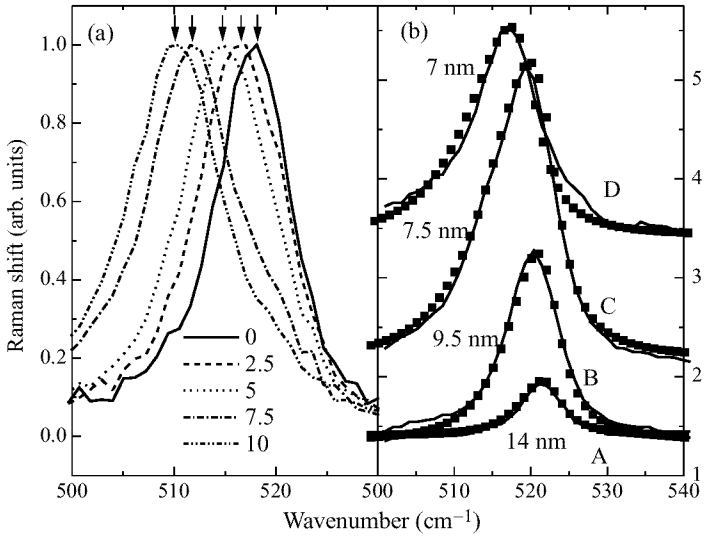


**Fig. 2.** Raman scattering spectra for the sample thermally annealed at 500°C: (a) changing laser focus distance (i.e. effective power) and, (b) measured after exposition to sample exposed during 6, 9, 12 and 15 min to a light intensity of 5 (A), 5 (B), 20 (C) and 20 (D) mW, respectively.

a high concentration of silanol bonds, even around the Si grains. So that the light bath can produce a chemical reaction that reduces the Si grain size. Also, the heating due light bath can produce intensive mechanical stresses on the silicon grains, so that the Raman peak shifts to lower values with the power intensity. The grain size reduction could be produced by a photo-chemical process like photo-oxidation of Si-Si bonds by the presence of Si-OH bonds. The small Si grains with sizes about 10 nm are irregular shapes with a great quantity of (-OH) ions linked to their surface. The weaker Si-Si bonds on the grain surface could easily be oxidized as effect of the light bath producing an effective reduction of the Si grain size. This mechanism is limited by the concentration of weak surface Si-Si bonds.

Nanometric sized particles produced by ball milling were introduced into $SiO_2$ matrix by the sol-gel method. $SiO_2$ matrix with high silanol concentration can be produced by a ball milling procedure of the sol-gel solution. The Si-OH concentration in this matrix can be kept for high temperatures as was proven by FT-IR spectroscopy measurements. Raman scattering measurements showed a reduction of Si grain size due light exposition which can be an evidence of a photo-chemistry process, or also to the presence of intensive stresses on the Si nanoparticles embedded into a $SiO_2$ matrix with high silanol concentration.

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